Insights into the interaction between CH_2F_2 and titanium dioxide: DRIFT spectroscopy and DFT analysis of the adsorption energetics

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Abstract

Difluoromethane (CH_2F_2, HFC-32) has been proposed as a valid replacement for both CFCs and HCFCs (in particular HCFC-22), and nowadays it is widely used in refrigerant mixtures. Due to its commercial use, in the last years, the atmospheric concentration of HFC-32 has increased significantly. However, this molecule presents strong absorptions within the 8 - 12 μm atmospheric window, and hence it is a greenhouse gas which contributes to global warming. Heterogeneous photocatalysis over TiO_2 surface is an interesting technology for removing atmospheric pollutants since it leads to the decomposition of organic compounds into simpler molecules. In the present work, the adsorbate-substrate interaction between CH_2F_2 and TiO_2 is investigated by coupling experimental measurements using DRIFT spectroscopy to first-principle simulations at DFT/B3LYP level. The experimental results confirm that CH_2F_2 interacts with the TiO_2 surface (~ 80% rutile, 20% anatase) through both F and H atoms and show that the DRIFT technique is well suited to study the adsorption of halogenated methanes over semiconductor surfaces. DFT calculations are carried out by considering different periodicities and surface coverages, according to a structure involving an acid-base interaction between the F and Ti^{4+} atoms as well as an H-bond between the CH_2 group and an O^{2-} ion. Lateral effects and energetics are analyzed in the limit of low coverage according to a procedure taking into account the binding, interaction, and distortion energies. The simulation at the different surface coverages and periodicities suggests similar decomposition pathways for the different investigated ensemble configurations.

Keywords: Difluoromethane; TiO_2; adsorption; density functional theory; lateral effects.

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1. Introduction

On the last decades, the role of many atmospheric trace compounds on the global environment and climate change has been the subject of a lot of investigations since apparently different phenomena like acid rains, photochemical air pollution and changes in stratospheric ozone layer are associated to their presence. During the past years halogen-containing molecules have attracted a great deal of attention because of their alarming connection with stratospheric ozone depletion and global warming [1-3]. Hydrohalofluorocarbons have been among the first candidates to replace the CFCs in many applications since they are degraded more efficiently in the lower atmosphere due to the attack by hydroxyl radicals [1,2].

Difluoromethane (CH_2F_2, HFC-32) is a relatively non-toxic gas which has been proposed for CFC and HCFC (hydrochlorofluorcarbons) replacement in new refrigerant systems. Due to its atmospheric relevance, over the years this molecule has been the subject of several spectroscopic investigations, either experimental and theoretical (for an overview of the relevant literature see [4-13] and references therein). Recently, the vibrational spectrum of this molecule has been thoroughly studied by coupling Fourier transform infrared (FTIR) spectroscopy to high level *ab initio* calculations [14]. The obtained potential energy surface and dipole moment surface, in conjunction with the accurate experimental data obtained from laboratory measurements, have led to a detailed modeling of the spectroscopic properties of CH_2F_2 concerning vibrational energy levels, integrated intensities and vibrational mixing.

Although HFC-32 has zero ozone depletion potential, it has a significant global worming potential [15] and for this reason its removal from the air should be desirable. Heterogeneous photocatalysis on semiconductors, such as on titanium dioxide (TiO_2), represents an interesting approach since it leads to the decomposition of organic compounds into simpler molecules such as water and carbon dioxide [16-18]. The knowledge about the adsorbate-substrate interaction should allow an improvement of the catalytic performances since the adsorption of the compound is one of the key steps in the degradation process. The interaction with the surface may lead in fact to a variation of the molecular structure such as to the activation of some bonds through e.g. their weakening. Then, a prediction of the reaction mechanism pathways based on the variation of the structural parameters may help to develop more successful applications.

Infrared (IR) spectroscopy is a well established method to obtain experimental information related to the strengthen variation of molecular bonds through an analysis of the shift of the corresponding absorptions, while first-principles simulations allow to implement the experimental data through an investigation of the geometrical parameters, the involved energies and the comparison between computed and observed vibrational frequencies. Then, the coupling between IR spectroscopy and quantum-mechanical calculations is an important tool in the study of the adsorbate-substrate interaction.

There are different ways of applying IR spectroscopy to solids, the best known technique being the transmission measurement. Although widely and profitably used, this method suffers of some disadvantages for the investigation of chemical processes taking place on solid catalysts. These mainly arise from sample preparation, as the pressing procedure, employed for preparing pellets or self-supporting wafers, may let to structural modifications of the solid phase and, besides, gases can no longer flow freely through the catalyst thus limiting mass transport. Moreover, in the case of self-supporting wafer, the solid layer must be sufficiently thin in order to allow the radiation to be transmitted [19,20].

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy overcomes the drawbacks of transmission methods as the sample requires a minimal preparation and it can be directly employed in powdered form. In addition, a number of commercially affordable environmental reaction chambers is available, that allow a fine control of the experimental conditions. This technique is also more sensitive than transmission methods to species adsorbed on solids. As a consequence DRIFT spectroscopy is imposing itself as a powerful tool in surface chemistry and it is becoming the most effective technique for the study of processes taking place at the gas-solid interface (e.g. see Refs. 21-25).

In a previous work the adsorption of CH_2F_2 on TiO_2 was investigated through IR transmission spectroscopy and DFT calculations [26] and, based on the experimental and computational results, it was suggested that CH_2F_2 interacts with TiO_2 through both one of the F atoms and one of the H atoms.

In order to gain more information related to the lateral effects among adsorbed molecules and to determine the energies in the limit of low coverage, in the present work we performed the calculation at different surface coverage and periodicities. One of the aims is to gain insights on the most probable ensemble configurations at the different surface coverage by comparing the binding and interaction energies for different periodicities corresponding to the same surface coverage**.** The other aim is to investigate the possible presence of different pathways for the different surface coverages or ensemble configurations. Finally, the adsorption of CH_2F_2 on titanium dioxide is also reinvestigated experimentally by DRIFT spectroscopy down to the limit of 1000 cm^{-1}, in order to take advantage from the sensitivity of this technique for the study of surface processes, and critically examining its advantages and drawbacks for the study of the adsorption of this atmospheric organic pollutant on the TiO_2 catalyst.

2. Experimental details

DRIFT experiments were performed by using the Harrick Scientific Praying Mantis diffuse reflectance accessory equipped with an high temperature reaction chamber (Harrick Scientific HVC-DRP-5). This reaction chamber is made of stainless steel and it is enclosed with a dome with three windows, two of which are made of KBr in order to allow the spectrometer radiation to enter and exit the chamber, while the third UV quartz window can be used for viewing or irradiating the sample. Within the reaction chamber there is a temperature controlled sample stage with integral sample cup. This stage, which is thermally isolated from the outer chamber wall, incorporates a cartridge heater and a thermocouple. A water cooling jacket controls the temperature of the outer surface of the chamber and windows during high temperature operations. The reaction chamber is equipped with three gas ports for evacuating, pressurizing or flowing the gas through the sample.

During the experiments the chamber was connected to either a vacuum line and to the temperature controller (Harrick Scientific ATC-024-1) and the cooling ports were attached to water inlet/outlet. Gas handling operations were carried out by using a stainless steel vacuum line equipped with both a rotary and a diffusive pump (the latter backed in turn by a second rotary pump). Pressure measurements were performed by using two capacitance vacuum gauges (Alcatel model ARD 1002 and 1003 with a full scale range of 100 and 10 mbar, respectively), each with a quoted manufacturer's full scale accuracy of 0.15%. Spectra were recorded in the medium IR region on a Bruker Vertex 70 FTIR spectrometer equipped with an MCT detector, a globar source and a KBr beamsplitter. A total of 128 interferograms for both the sample and the background spectra were co-added and Fourier transformed into the corresponding reflectance spectra.

As titanium dioxide strongly absorbs the IR radiation around and below 1000 cm^{-1}, in the experiments carried out by using a pure TiO_2 sample (P25 Degussa, ~ 80% anatase and 20% rutile) the spectral region below c.a. 1100 cm^{-1} was inaccessible due to the cutoff of the semiconductor surface. For this reason measurements were also carried out by diluting TiO_2 in KBr, which represents an optically non-interfering matrix and further it minimizes the unwanted effects due to specular reflection [27]. In particular, a solid substrate composed of 30% TiO_2 and 70% of KBr was employed, as a tradeoff between having an adequate concentration of TiO_2 for an appreciable adsorption of CH_2F_2 and a sufficient signal-to-noise ratio in the spectral region down to 1000 cm^{-1}.

In order to remove water and impurities such as hydrocarbons, which arise from the contact of the TiO_2 with air, as well as to make experiments reproducible, the solid substrate (either pure TiO_2 or TiO_2/KBr mixture) was pre-treated at high temperature (400 ◦C) under dynamic vacuum for 2 hours and then it was re-oxidized with a mixture of O_2/N_2. The spectrum obtained after this pre-treatment was used as background for the recording of the spectrum of the adsorbed gas. Besides to the spectra of adsorbed CH_2F_2, those of the free molecule were also recorded. All measurements were carried at 296 K and the spectra of either free and adsorbed CH_2F_2 were acquired at a resolution of 4 cm^{-1}. The CH_2F_2 sample purchased by Aldrich with a stated purity of 99.7% was used without any further purification. Differential spectra were obtained by subtracting the spectrum of the free molecule from the adsorption one.

3. Computational details

All the calculations have been performed using the CRYSTAL program [28]. The study was performed within the same computational conditions employed for previous work on CH_2F_2 [26].

In particular, the calculations were performed at DFT/B3LYP level [29,30] and an 86-51G* and 8-411G contractions properly developed for the TiO_2 surface were adopted for the O and Ti atoms, respectively [31]. For the molecule, the cc-pVTZ contraction was used [32].

In order to take into account the anharmonicity, the present calculated frequencies were scaled by using a scaling factor equal to 0.965 which was obtained by the NIST [33] for the method and basis set adopted for the CH_2F_2 molecule.

The adsorption was simulated at four different surface coverages (θ) and six different periodicities ($n \times m$) which define the surface unit cells of dimension $n\mathbf{a}$ and $m\mathbf{b}$, where $\mathbf{a}$ and $\mathbf{b}$ are the lattice vectors of the primitive surface cell. In particular, the adsorption was investigated at θ equal to 1ML (monolayer), 0.5ML, 0.33ML and 0.25ML and the ($n \times m$) periodicities were taken equal to (1 x 1), (1 x 2), (1 x 3), (2 x 1), (3 x 1) and (2 x 2). (1 x 2) and (2 x 1) correspond both to 0.5ML and (1 x 3) and (3 x 1) correspond both to 0.33ML.

3. Results and discussion

3.1. *DRIFT Spectra*

The differential spectrum of CH_2F_2 adsorbed on TiO_2 is presented in Figure 1, together with the spectrum of the free molecule. In discussing the shifts of CH_2F_2 vibrational frequencies observed upon adsorption, which in turn mirror the structural modifications induced by the interaction with the semiconductor surface, it is convenient to start from the higher wavenumber region, around 3000 cm^{-1}. In the spectrum of the free molecule, this region deals with the absorptions due to the ν_1 (2948 cm^{-1}) and ν_6 (3014 cm^{-1}) normal modes, corresponding to symmetric and asymmetric CH_2 stretching, respectively. In the spectrum of the adsorbed molecule, both bands are blue shifted by about 5 cm^{-1}. The observed frequencies of 2955 cm^{-1} and 3019 cm^{-1} are in perfect agreement with those obtained from the transmission measurements performed on a self-supporting wafer [26]. Further, from DRIFT experiments an additional weaker band can be observed at 2835 cm^{-1}, which is consistent with the first overtone of the ν_8 band of the adsorbed molecule. The ν_8 fundamental, arising from the CH_2 wagging vibration, gives rise to a band at 1436 cm^{-1} in the free compound which is shifted to 1431 cm^{-1} when the CH_2F_2 adsorbs on TiO_2. In previous transmission measurements, this band was assigned at 1423 cm^{-1}, yet, taking into account the spectral resolution and the somewhat different solid substrates employed, there is substantial agreement with the present DRIFT results. Further, according to the transmission spectra, a band at 1496 cm^{-1} was assigned as the ν_2 fundamental, blue-shifted by 12 cm^{-1} with respect to the free gas phase molecule. In the differential DRIFT spectra this absorption appears as a weak band at 1498 cm^{-1}, whose band contour is rather irregular due to the interference, in this spectral region, of ro-vibrational transitions belonging to the wing of the water vapor ν_2 band. The last region to consider, between 1000 and 1250 cm^{-1}, is quite complex because of the TiO_2 cutoff as well as the presence of the very strong ν_3 and ν_9 bands, which give rise to a continuum between 1040 and 1200 cm^{-1}. In the free molecule, these two bands, which are mostly responsible for the radiative forcing of CH_2F_2, are located at 1112 (ν_3) and 1090 (ν_9) cm^{-1} and correlate to CF_2 symmetric and asymmetric stretching vibrations. Analysis of the differential spectra obtained from DRIFT experiments, suggests that, in the adsorbed molecule, the ν_3

vibration blue shifts to 1124 cm^{-1}, while the ν_9 vibration seems to be red shifted by about 60 cm^{-1}, giving rise to a weaker band at 1030 cm^{-1}. At this point is should be noted that for the band at 1124 cm^{-1} there is a perfect agreement to transmission measurements, whereas the 1030 cm^{-1} absorption appears well resolved only in DRIFT spectra. Rather a band at 972 cm^{-1} was identified in the spectra derived from CH_2F_2 adsorption on the TiO_2 self-supporting wafer. Unfortunately, this spectral region was not reliably accessible in the DRIFT spectra measured in this work. In any case, the features appearing in the differential spectra around and below 1000 cm^{-1} must be taken with care, because the low S/N ratio due to the TiO_2 cutoff and the very strong bands of the free molecule makes difficult the identification of underneath absorptions due to the adsorbed species. Besides, from the computational modeling of CH_2F_2 adsorption on TiO_2 the ν_9 band is expected to be appreciably shifted to lower wavenumbers with respect to the free molecule, and this is confirmed experimentally. It should be noted that the presence of two absorptions for the C-F stretching can be due to two different strengths for the acid-base interaction. The lowest absorption may be due to a stronger adsorbate-substrate interaction, while the highest absorption should arise from the adsorption at high surface coverage, which leads to a destabilization of the adsorbed molecule as found for the net interaction energy (see later Table 3) at θ equal to 1ML. In transmission measurements a shoulder was observed at 1164 cm^{-1}, also appearing in the DRIFT spectrum as a weak band, probably due to the ν_7 vibration of adsorbed CH_2F_2. In the free molecule, this vibration, corresponding to the CH_2 rocking normal mode, gives rise to a c-type band at 1179 cm^{-1}. Finally, another weak band, located at 1202 cm^{-1}, can be identified in the DRIFT spectrum of Figure 1. This frequency compares favorably with the value of 1223 cm^{-1} calculated for the ν_5 band and hence it can be tentatively assigned to the ν_5 normal mode of the adsorbed molecule. It should be pointed out that in the free molecule the ν_5 vibration, corresponding to the CH_2 twisting, is expected to be IR inactive because it belongs to the A_2

symmetry species. Nevertheless, it gives rise to a very weak band as a consequence of the mixing between the $v_5 = 1$ and $v_7 = 1$ states induced by a strong c-type Coriolis resonance [13,14]. On the other hand, when the molecule is adsorbed this vibration should produce a nearly-forbidden band also as a consequence of the symmetry breaking caused by the interaction with the surface. The fundamental vibrational frequencies of CH_2F_2 adsorbed on TiO_2 obtained from DRIFT experiments are summarized in Table 1, together with the computed ones (see later). For completeness the v_9 value from transmission spectra is also reported in this table.

Summarizing there is, in general, a close agreement between the adsorption spectra obtained from DRIFT and transmission measurements. Thus, the band shifts observed experimentally suggest that the CH_2F_2 molecule interacts with the TiO_2 surface through both F and H atoms. The present measurements also show that DRIFT spectroscopy can be profitably used to study the adsorption of fluorinated organic pollutants on the surface of the TiO_2 catalyst, that can be used directly in a powdered form with a minimal sample preparation. Nevertheless, in order to access the spectral region around 1000 cm^{-1}, the semiconductor has to be diluted in a KBr matrix.

3.2. DFT calculations

As reported in the experimental details, the TiO_2 sample is composed by 80% of anatase and 20% of rutile. Since the anatase (101) surface is the most stable, it should be the most exposed surface available for the adsorption. On this basis, we considered the anatase surface along the (101) plane, modeling it with a 30-atomic layers slab cut from the optimized bulk.

The analysis of the adsorbate-substrate interaction is based on the adsorption structure involving the interaction between the F atom and the Ti(5*f*) ion and the H-bond between the CH_2

group and the O(2*f*) ion. This structure was chosen for analyzing the lateral effects and energetics of the adsorption because it resulted to provide the better agreement to the experimental data obtained from transmission spectra. Indeed, quantum chemical calculations on the CH_2F_2 - TiO_2 system were already performed in a previous work [26], where the frequencies calculated for three different adsorbate - substrate structures (namely, I, II and III) were compared with transmission measurements.

Table 2 summarizes the most important geometrical parameters for the systems under investigation; the percentage deviations (%) of the molecular parameters with respect to the optimized isolated molecule are also reported in the same Table. Upon the adsorption, there is an increase of the C—F bond length related to the F atom involved in the adsorption and to a decrease for the other C – F bond length. This should mean that the first C—F bond becomes weaker while the other becomes stronger. Both the two C—H bond lengths decrease upon the adsorption as effect of the variation in the C—F bonds. Is it interesting to notice that the C—H bond length related to the H involved in the H-bond with the surface decreases differently to what is commonly expected. This behaviour may be due to the fact that the molecule is also interacting with the surface Lewis acid site through one of the halogen atoms so the molecule has to modify the geometry to arrange with both the two types of surface Lewis sites. As consequence of the adsorption, the F–C–F bond angle decreases while the H–C–H one increases. In general, based on the variation of the structural parameters, we could suggest that the adsorbate-substrate interaction leads to an activation of the C—F bond involved in the adsorption. This should represent the first step in the decomposition process of CH_2F_2 on TiO_2, that is likely to proceed through the C—H bond breaking. Since the magnitude of the variation of the C—F bond length is about constant for all the investigated systems, we could also suggest a common degradation pathway for all the considered ensemble configurations.

Before moving to the results obtained for the energetics of the CH_2F_2 adsorption process on TiO_2, the comparison between experiment and theoretical model deserves a few comments. One of the main features predicted by the calculations is the blue shift of both the CH_2 stretching vibrations, which is indeed confirmed experimentally. Concerning the magnitude of the shifts, one should consider that errors of tenths of wavenumbers are expected for vibrational frequencies computed at DFT/triple-ζ basis set level, even for the simpler case of the free molecule [13]. In this respect, it is worth noting that the vibrational frequencies computed for the adsorbate-substrate system are closer to the experimental ones than those of the free molecule. Further, it should be taken into account that anharmonic effects are modeled on an average way only (i.e. by means of scaling factors), though this approach neglects important effects, such as anharmonic resonances. On the other hand, full anharmonic computations, i.e. the calculation of cubic and quartic force constants, are not affordable for systems like those here investigated, and therefore one is forced in resorting to approximated approaches, like scaled harmonic frequencies. A last point to consider is the complexity of the system investigated experimentally; for polyatomic molecules different adsorption pathways are possible, with binding energies different by just a few of kJ mol^{-1} (see Ref. [26]), hence laboratory experiments are actually carried out on the ensemble average over the possible interaction configurations. Under this point of view, quantum chemical simulations describe a simplified system (e.g. one adsorption configuration, one adsorption site,...). Nonetheless they provide fundamental information for the correct interpretation of the experimental observations. In this respect, despite the underlying approximations of the computational modeling and the complexity of the adsorbate-substrate system investigated, the main features described by the proposed adsorption model, i.e. the frequency shifts of CF_2 and CH_2 stretching, are confirmed by the laboratory measurements.

The energetic of the adsorption were investigated by the computation of the binding (*BE)*, interaction (E_{int}) and distortion (E_{dis}) energies where *BE* is equal to the difference in stability of the adsorbate-substrate system with respect to the separated components, i.e. the isolated optimized molecule and surface; E_{int} represents the difference in stability between the final system and the two components at their distorted geometry; E_{dis} is associated to the energy due to the variation of the geometry upon the adsorption. Based on the procedure described elsewhere [34], three types of energy are associated to *BE*, E_{int} and E_{dis} , namely the periodic, lateral and net energies. The periodic energies refer to the adsorption of the monolayer of molecules; the lateral energies take into account the lateral effects between co-adsorbed molecules, and the net energies are related to the adsorption of a single molecule and correspond to the sum of the periodic and lateral energies. For clearness all the equations used for the calculations of the different energies are given in Appendix A.

The values of all the obtained energies are reported in Table 3 and those of E_{int} and *BE* were corrected for the basis set superposition error (BSSE) based on to the counterpoise method [35]. Table 3 shows that the value of the periodic E_{int} (E^{P}_{int}) is smaller in absolute value for the (1 x 1) periodicity with respect to the other unit cells. The lateral E_{int} (E^{L}_{int}) is strongly attractive for the (1 x 2) and (1 x 3) cases and moderately repulsive for the other one, except for the (2 x 2) unit cell. The periodic E_{dis} (E^{P}_{dis}) is almost constant for all the periodicities except for the (1 x 1) one. In general, the periodic *BE* (BE^{P}) is bigger in absolute value for the (*n* x 1) and (2 x 2) periodicities with respect to the (1 x *m*) ones. The lateral *BE* (BE^{L}) is largely negative for the (1 x 2), (1 x 3) and (2 x 2) cases and positive for the other ones. Considering the net E_{int} (E^{N}_{int}) the biggest (unsigned) value is observed for the (1 x 3) periodicity while the smallest one is found for the (1 x 1) unit cell. This is reflected in the net *BE* (BE^{N}).

In order to analyze the effects due to the repulsion or attraction between co-adsorbed molecules, we determined the interaction constants, both direct and surface-mediated, and the energies in the limit of an isolated adsorbed molecule using the procedure reported elsewhere [34].

In particular, we calculated the direct interaction constants (*i*) as:

$$E_{\mathrm{int}}^{L} = i_{na} + i_{mb} + 2i_{na,mb} \tag{1}$$

where the constants are labeled with the subscripts *na* and *mb* indicate the constant between a molecule and another molecule placed in two adsorption sites separated by *n***a** and *m***b**, respectively. The subscript *na,mb* is related to the constant between molecules separated by the diagonal vector (**a**,**b**). A positive (negative) value of the constant i means that there is a direct repulsion (attraction) between the two neighboring molecules.

The surface-mediated interaction constants (*I*) and the interaction energy in the limit of an isolated adsorbed molecule ($E_{\mathrm{int}}^{\mathrm{lim}}$) are obtained as:

$$E_{\mathrm{int}}^{P} = E_{\mathrm{int}}^{\mathrm{lim}} + (I_{na} + I_{mb} + 2I_{na,mb}) \tag{2}$$

As for i, a positive (negative) value of the constant I means that there is a surface-mediated repulsion (attraction) between the two neighboring molecules.

The distortion and binding energies in the limit of an isolated adsorbed molecule (E_{dis}^{lim} and BE^{lim}, respectively) are computed by analogy with Eqn. (2).

The obtained values of the different *i* and *I* are reported in Table 4 and the CH_2F_2 configurations at the different periodicities are shown in Figure 2. The reported values indicate that there is a strong direct attraction and a surface-mediated repulsion along the **a** direction. We suggest that the direct attraction comes from the interaction between F and H atoms and decreases at the increase of the F - H distance. Along the **b** direction there is repulsion due to both the direct and surface-mediated effects; the direct repulsion may be originated by the influence of the below surface on the electronic properties of the F and H atoms involved in the adsorption. In general, the strong direct attraction F – H along the **a** direction explains the large attractive lateral interaction energy observed for the (1 x 2) and (1 x 3) periodicities. Similarly the direct repulsion along the **b** direction explains the repulsive lateral interaction energy for the (2 x 1) and (3 x 1) periodicities. The resulting effects are nearly balanced for the (1 x 1) and (2 x 2) periodicities which are affected by both the attraction and repulsion between neighbouring molecules.

The values of the interaction, distortion and binding energy in the limit of an isolated adsorbed molecule are equal to -32.4, 13.9 and -18.5 kJ/mol, respectively. Different from other CH_2FX (where X = Cl and Br), we can see that the value of $E_{\mathrm{int}}^{\mathrm{lim}}$ is close to the value of the net interaction energies associated to the (1 x 2) and (1 x 3) periodicities as well as to that of the (2 x 2) periodicity. Looking at BE^{lim}, its value is very close to that of the (2 x 2) periodicity and it is underestimated or overestimated with respect to the value for the (*n* x 1) and (1 x *m*) periodicities, respectively. This means that the (2 x 2) periodicity can well simulate the case of an isolated adsorbed molecule while for the (1 x *m*) periodicities there is an additional positive contribution due to the direct attraction along the **a** direction. By contrast, the (*n* x 1) periodicities are influenced by the negative contribution due to the repulsion, both direct and surface-mediated, along the **b** direction. Since the (2 x 2) periodicities well represent the case of low coverage, we used the corresponding geometry to compute the vibrational frequencies reported in Table 1.

In general, it is found that at coverage 0.5ML and 0.33ML the most probable ensemble configurations are those related to the (1 x *m*) periodicities instead of the (n x 1) periodicities. This finding differs completely from that inferred for CH_2ClF [37] and CH_2BrF [38] and this behaviour suggests that the interactions between neighbouring molecules involved in an adsorption process cannot be deduced a priori, even if the adsorbate belongs to the same class of compounds (CH_2XF). The interaction constants are also different from those associated to CH_2CHF adsorbed on the same surface [39], confirming that the analysis on the lateral effects is an important tool in order to better understand the experimental results.

4. Conclusions

The adsorption of CH_2F_2 over TiO_2 has been investigated both experimentally and theoretically by coupling DRIFT spectroscopy to DFT periodic simulations. On the experimental side, the analysis of the DRIFT differential spectrum, has led to the assignment of the vibrational absorption bands of the adsorbed molecule, showing that CH_2F_2 interacts with the TiO_2 surface by means of either fluorine and hydrogen atoms. The results have been compared to those previously obtained from transmission measurements, showing a perfect agreement between the two techniques, and thus demonstrating that DRIFT spectroscopy can be employed profitably for studying the adsorption of halogenated methanes on the TiO_2 surface with the advantage of a minimal sample preparation. Theoretically, we investigated the lateral effects and the energies in the limit of low coverage of CH_2F_2 adsorbed on TiO_2 simulating the adsorbate-substrate interaction through an acid-base interaction between the F and Ti atoms as well as an H-bond between the CH_2 group and an O ion. We found that the adsorption leads to the activation of the C—F bond involved in the adsorption. The simulation at the different surface coverages and periodicities suggests similar decomposition pathways for the different investigated ensemble configurations. The analysis of the interaction, distortion and binding energies as well as of the interactions between co-adsorbed molecules shows a different behavior of the molecule with respect to CH_2FCl and CH_2FBr confirming that the study of the lateral effects is an important tool to better understand the experimental results also in the case of adsorbates belonging to the same class of compounds (e.g. CH_2XF).

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Appendix A

The periodic (indicated by the superscript *P*), lateral (indicated by the superscript *L*) and net (indicated by the superscript *N*) interaction energies were calculated respectively as:

$$E_{\mathrm{int}}^{P} = E_{sys} - (E_{mon\backslash sys} + E_{sur|sys}) \tag{A.1}$$

$$E_{\mathrm{int}}^{L} = E_{mon|sys} - E_{mol|sys} \tag{A.2}$$

$$E_{int}^{N} = E_{int}^{P} + E_{int}^{L} = E_{sys} - (E_{mol|sys} + E_{sur|sys}) \tag{A.3}$$

The periodic, lateral and net distortion energies were calculated respectively as:

$$E_{dis}^{P} = (E_{mon|sys} - E_{mon}) + (E_{sur|sys} - E_{sur}) \tag{A.4}$$

$$E_{dis}^{L} = (E_{mol|sys} - E_{mol}) - (E_{mon|sys} - E_{mon}) \tag{A.5}$$

$$E_{dis}^{N} = E_{dis}^{P} + E_{dis}^{L} = (E_{mol|sys} - E_{mol}) + (E_{sur|sys} - E_{sur}) \tag{A.6}$$

The periodic, lateral and net binding energies were calculated respectively as:

$$BE^{P} = E_{int}^{P} + E_{dis}^{P} = E_{sys} - (E_{mon} + E_{sur}) \tag{A.7}$$

$$BE^{L} = E_{int}^{L} + E_{dis}^{L} = E_{mon} - E_{mol} \tag{A.8}$$

$$BE^{N} = BE^{P} + BE^{L} = E_{int}^{N} + E_{dis}^{N} = E_{sys} - (E_{mol} + E_{sur}) \tag{A.9}$$

where E_{sys}, E_{mon}, E_{mol} and E_{sur} are the optimized energies of the system, monolayer of adsorbed molecules, isolated molecule and surface, respectively, while $E_{mon|sys}$, $E_{mol|sys}$ and $E_{sur|sys}$ are the energies of the monolayer, the isolated molecule and the surface calculated at the optimized geometry of the adsorbate-substrate system.

Based on Eqns. (A.1) and (A.3) a negative (positive) value of E_{int} means that there is attraction (repulsion) between the molecule and the surface. According to Eqns. (A.7) and (A.9) a negative (positive) value of *BE* means that the adsorption is a favorable (unfavorable) process.

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Figure captions

Fig. 1. (a) Vibrational spectrum of gas-phase CH_2F_2 between 970 and 3250 cm^{-1} showing the relevant fundamental vibrations. (b) Differential DRIFT spectrum of CH_2F_2 adsorbed on TiO_2 between 970 and 3250 cm^{-1}. The band assignment, based on the correspondence to CH_2F_2 normal modes, is reported. Arrows indicate the frequencies predicted by B3LYP/cc-pVTZ computations (ν_i^{dft}).

Fig. 2. (a)-(f) CH_2F_2 adsorbed on the anatase TiO_2 (101) surface at different periodicities (*n* x *m*): (a) (1 x 1); (b) (1 x 2); (c) (1 x 3); (d) (2 x 2); (e) (2 x 1); (f) (3 x 1). The surface has been omitted from the figure. (a)-(f) were obtained using VESTA program [36].

Table 1. Experimental and computed fundamental frequencies of CH_2F_2 in the gas phase and adsorbed on TiO_2.

Symmetry Species	Normal Mode	Approximate Description	CH_2F_2 adsorbed on TiO_2 [a]		Gas phase CH_2F_2		Ads – free	
			Experimental	B3LYP/ cc-pVTZ	Experimental [b]	B3LYP /cc-pVTZ [c]	Experimental	B3LYP/ cc-pVTZ
A_1	ν_1	CH_2 symmetric stretch	2955	2968	2947.9	2942	+7	+26
	ν_2	CH_2 scissor	1498	1476	1509.60	1478	-11	-2
	ν_3	CF_2 symmetric stretch	1124	1094	1111.61	1071	+12	+23
	ν_4	CF_2 bend	n.o.[d]	495	528.34	508	-	-13
A_2	ν_5	CH_2 twist	1202[e]	1223	1256.8	1227	-54	-4
B_1	ν_6	CH_2 asymmetric stretch	3019	3061	3014.45	3007	+5	+54
	ν_7	CH_2 rock	1164	1148	1178.74	1144	-15	+4
B_2	ν_8	CH_2 wag	1431	1391	1435.5	1409	-5	-18
	ν_9	CF_2 asymmetric stretch	(1030, 972[f])[e]	930	1089.9	1043	(-60, -118[f])[e]	-113

[a] Present work.

[b] From Ref. [14].

[c] Scaled harmonic frequencies of vibration from Ref. [26].

[d] Not observable due to TiO_2 cutoff.

[e] See discussion in the text.

[f] From transmission spectra on TiO_2 self supporting wafer [26].[g]

Table 2. Main structural parameters for the CH_2F_2 – anatase TiO_2 (101) system [a].

		%exp	**(1 × 1)**	%	**(1 × 2)**	%	**(1 × 3)**	%	**(2 × 1)**	%	**(3 × 1)**	%	**(2 × 2)**	%
C-F_1	1.361	0.2	1.402	3.0	1.399	2.8	1.399	2.8	1.409	3.5	1.406	3.3	1.407	3.4
C-F_2	1.361	0.2	1.352	-0.7	1.350	-0.8	1.352	-0.7	1.348	-1.0	1.349	-0.9	1.347	-1.0
C-H_1	1.091	-0.1	1.084	-0.6	1.085	-0.5	1.086	-0.5	1.086	-0.5	1.087	-0.4	1.087	-0.4
C-H_2	1.091	-0.1	1.085	-0.5	1.085	-0.5	1.084	-0.6	1.087	-0.4	1.087	-0.4	1.087	-0.4
F_1-C-F_2	108.7	0.5	106.8	-1.7	107.3	-1.3	107.1	-1.5	106.7	-1.8	107.0	-1.6	107.1	-1.5
H_1-C-H_2	113.1	1.4	113.9	0.7	114.5	1.2	114.7	1.4	115.5	2.1	115.9	2.5	116.1	2.7
F_1-Ti(s)			2.347		2.313		2.306		2.288		2.285		2.270	
H_1-O(s)			2.467		2.372		2.305		2.142		2.162		2.202	
C-F_1-Ti(s)			117.2		120.6		122.5		123.2		122.7		122.8	
C-H_1-O(s)			97.8		107.1		111.9		123.5		123.4		122.2	

[a] bond lengths and angles are given in angstroms and degrees, respectively. % refers to the variation with respect to the isolated optimized molecule.

Table 3. Adsorption energetics for the CH_2F_2-anatase TiO_2 (101) system [a].

	1 × 1	**1 × 2**	**1 × 3**	**2 × 1**	**3 × 1**	**2 × 2**
E_{int}^{P}	-20.01	-23.64	-26.17	-27.24	-27.63	-29.44
$E_{dis}^{P,mon}$	2.75	3.28	4.06	4.28	4.48	5.35
$E_{dis}^{P,sur}$	3.87	5.16	6.43	5.71	5.79	6.19
E_{dis}^{P}	6.62	8.44	10.49	9.99	10.26	11.55
BE^{P}	-13.40	-15.19	-15.68	-17.25	-17.37	-17.89
E_{int}^{L}	0.74	-4.50	-5.68	2.72	1.70	-0.18
E_{dis}^{L}	0.39	-0.51	-1.06	0.26	-0.33	-1.20
BE^{L}	1.12	-5.01	-6.75	2.99	1.37	-1.38
E_{int}^{N}	-19.28	-28.14	-31.86	-24.52	-25.93	-29.61
E_{dis}^{N}	7.01	7.93	9.43	10.25	9.94	10.35
BE^{N}	-12.27	-20.21	-22.43	-14.27	-15.99	-19.27

[a] energies are in kJ mol^{-1}. The formulas for the different energies are given in Appendix A.

Table 4. Direct (*i*) and surface-mediated (*I*) interaction constants for the CH_2F_2-anatase TiO_2 (101) system [a].

	1**a**	2**a**	1**b**	2**b**	1**a**,1**b**	2**a**, 2**b**
I	6.2	0.4	4.7	2.5	0.7	--
i	-5.7	-1.4	1.7	1.2	2.4	1.2

[a] constants are in kJ mol^{-1}.